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Ammonia Removal from Wastewaters Using Natural Australian Zeolite. I. Characterization of the Zeolite

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ABSTRACT

This study considered the potential of a natural Australian zeolite, clinoptilolite, to remove ammonium from water. Ammonium-exchange capacity and rates of adsorption are critical to the assessment of the feasibility of the zeolite for application to continuous wastewater treatment. A laboratory study was undertaken, using pure solutions, to investigate the equilibria and kinetic characteristics of ammonium exchange in the zeolite. Binary equilibrium experiments provided information on the adsorption characteristics of the zeolite in terms of ammonia capacity at varying solution concentrations. These experiments also revealed that the highest ammonium removal efficiency was achieved when the zeolite's exchange sites were converted to the sodium form. Multicomponent equilibrium experiments were carried out to determine the effects of competing cations on the ammonium-exchange capacity of the zeolite. The laboratory study indicated the zeolite's selectivity for ammonium ions over other cations typically present in sewage (calcium, magnesium, and potassium), and provided information relevant to the design and operation of a continuous process.

INTRODUCTION

Most high-rate physicochemical sewage treatment processes are very efficient at removing suspended solids, phosphorus, oil and grease, and heavy metals, but are unable to reduce the soluble ammonium concentration. In or-

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der to comply with the increasingly strict limits being placed on ammonia levels in sewage discharged into receiving waters, a high-rate ammonia removal process is needed to supplement these existing processes. For such an ammonia removal process to be viable, it must be capable of reducing sewage ammonium concentrations from 20–60 mg/L down to 5 mg/L. This must be achieved at a minimal cost if the process is to be competitive with conventional biological treatment. Of the high-rate ammonia removal processes available, selective ion exchange using natural zeolite offers a number of distinct advantages:

- The natural zeolite, clinoptilolite, is highly selective for ammonium ions, compared with most other cations typically present in sewage
- The efficiency of ion exchange by the zeolite is relatively independent of temperature
- Ammonia removal by ion exchange is not coupled with increases in dissolved suspended solids

Natural zeolites, from deposits in the United States, Hungary, Japan, and Korea, have been shown to achieve high ammonium removal efficiencies at relatively low cost. However, there is a significant variation in the ion-exchange characteristics and structural rigidity of clinoptilolites from different sources. The potential of Australian natural zeolite for application to continuous sewage treatment is not known. Extensive investigations have been made, using zeolites from several countries, to ascertain the optimum operating conditions for removal of ammonia from wastewaters. From the results of these studies it is apparent that the potential for using Australian clinoptilolite for ammonium removal from sewage depends upon:

- Ammonium equilibrium and total capacity of the zeolite
- The effect of competing cations present in the sewage on the exchange equilibria and kinetics
- The rate-determining step in the ammonium exchange onto the zeolite
- Whether the zeolite can be fully regenerated so that the total ammonium exchange capacity (AEC) may be restored. If regeneration is achievable, under what conditions will this be best accomplished?

BACKGROUND

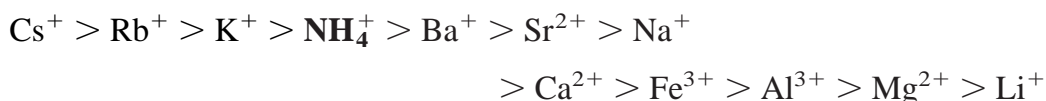
Zeolites are crystalline aluminosilicates enclosing pores occupied by cations and water molecules, permitting reversible ion exchange and reversible dehydration (1). Clinoptilolite is a natural zeolite. The cationic makeup of the aluminosilicate consists of aluminum ions (Al^{3+}) in a predominantly Si framework (an aluminosilicate). The charge imbalance resulting from the substitution of aluminum atoms for silicon atoms requires a nearby



cation to preserve electrical neutrality, so the cation content is directly related to the Al content. In nature, these cations are typically Na^+ , Ca^{2+} , Mg^{2+} , or other alkaline earth elements (1).

Fredrickson (2) noted that the cation selectivity was different for each zeolite, and that clinoptilolite is highly ammonium-ion selective. This is due to the size and charge of the hydrated cation and specific crystal structure of, and distribution of, the exchange sites in the zeolite. He concluded that the zeolite-exchange selectivity depends on its particle size, shape, uniformity, purity, and consistency. Due to their regular, uniform structure, zeolites exclude ions by an "ion sieve" action (3), and the degree of exclusion is specific for each zeolite.

In the 1950s, Ames (4) determined the ion selectivity for clinoptilolite as:



Those cations which are more amenable to selection by clinoptilolite are not commonly found in municipal sewage streams, except for potassium (5). Clinoptilolite's unusual selectivity for NH_4^+ ions is caused by structurally related ion sieve properties found to differing degrees in many zeolites (5). Koon and Kaufman (5) have shown that the extent of ion sieving depends on:

- The size of openings into the ion cages contained in the 3-D lattice structure
- The energy or strength of bonding between the water and zeolite framework

For clinoptilolite, the pore diameters vary from around 0.45 to 0.6 nm (6), and these pores dictate the size of ions that can enter the clinoptilolite pores and undergo ion exchange. The effective pore size of the clinoptilolite may be altered by varying the exchanging cation, since the clinoptilolite is not completely rigid, and this leads to varying cation-exchange capacities for clinoptilolite subjected to different pretreatment conditions. The main components in the natural clinoptilolite structure, as given by Howe (6), are presented in Fig. 1. The crystal lattice comprises channels of two different sizes, and each type may display a different selectivity behavior for certain cations. Barrer et al. (3) noted that movement into and along one set of channels is governed by elliptical windows having approximate dimensions of 7.9 Å by 3.5 Å; the other channels have a set of windows with dimensions of about 4.4 Å by 3.0 Å.

Barrer et al. (3) claimed that the ion sieve exclusion from these latter channels occurred for large ions, and clinoptilolite can exercise a double sieve action. The separate ion sieve effects of the two kinds of channel or pore size in



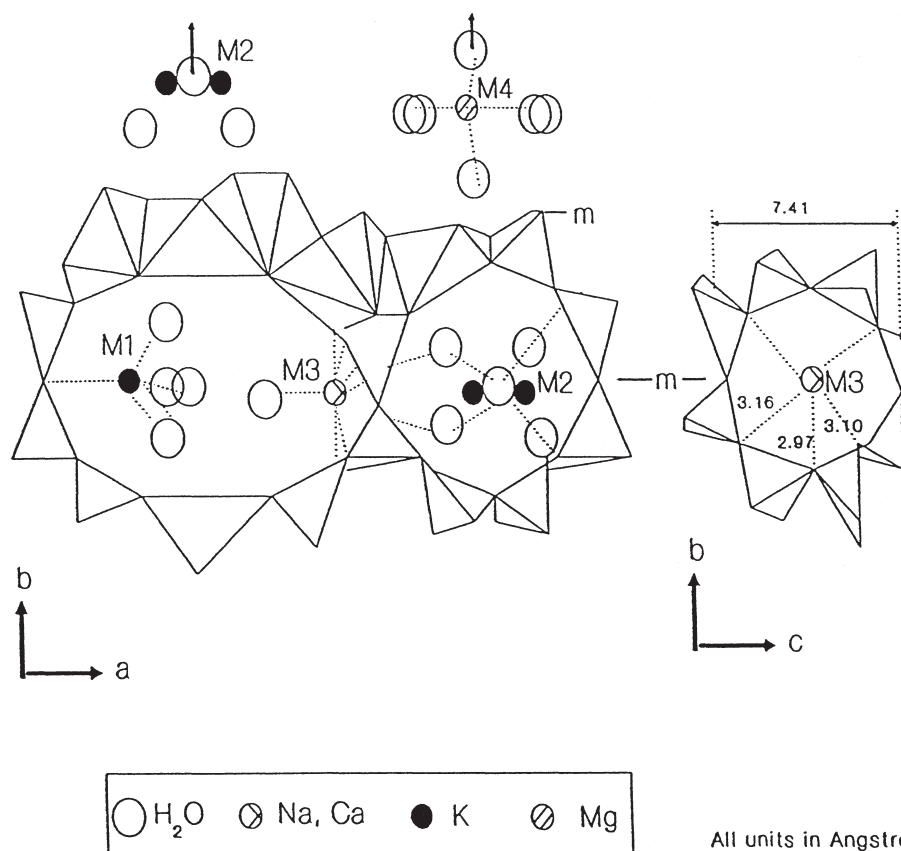
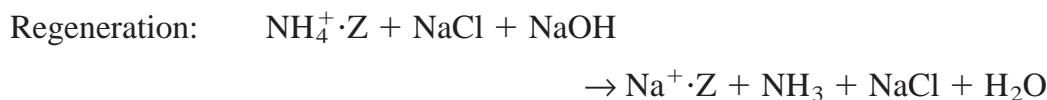
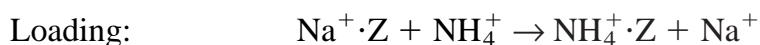


FIG. 1 Main components of the clinoptilolite structure, as presented by Howe (6), where M1 to M4 describe the molecular bonds between earth elements and water within the zeolite crystal.

the clinoptilolite, and the free dimensions of these channels, allow a cation of a particular size to access none, one, or both of the channels for exchange. Hence the degree of exchange is specific for each clinoptilolite with each cation in solution. Koon and Kaufman (5) expressed the loading and regeneration of the sodium form of clinoptilolite, where Z represents the zeolite, as:



Column studies by McLaren and Farquhar (7) concluded that the ammonium-exchange capacity of their California clinoptilolite is most affected by the initial ammonium ion concentration of the solution to be treated. The breakthrough volume was increased by a factor of 2.5 when the influent con-



centration was decreased from 70 to 14 mg N/L. Other factors such as temperature and flow rate through the bed had a much less significant impact on the breakthrough capacity of the system.

EXPERIMENTAL TECHNIQUE

Preconditioning of the Zeolite

Characterization of the zeolite in terms of equilibria was undertaken to determine its value as an ammonium selective exchanger. Past literature revealed that the ammonium adsorption capacity of the zeolite was dependent upon its cationic form or pretreatment conditioning. It was considered valuable to assess the saturation capacity of the zeolite first, both in its "as received" or "virgin" state and after conversion to various cationic forms. Pretreatment conditioning was achieved by contacting samples of each size fraction of the zeolite with 20 g/L chloride salts of sodium, calcium, magnesium, and potassium. The solutions used for preconditioning the zeolite were made up from analytical grade chloride salts dissolved into deionized water. Hydroxides of the metals were added in dilute form to raise the solution pHs to 11 to expedite conversion of the zeolite to the particular cationic form. These were performed in 250 mL conical flasks. A sample procedure is given for the zeolite preconditioning to the sodium form:

1. 10 g of each zeolite size fraction taken for preconditioning
2. Each fraction washed three times with 100 mL volumes of distilled water
3. Each fraction placed in conical flask with 100 mL solution of 20 g/L of analytical grade NaCl
4. Added 2 M NaOH to raise solution pH to 11. Rubber stopper fitted securely to flask
5. Placed on shaker table overnight in constant temperature room at 20°C
6. After 24 hours contact, decanted off caustic brine solution and replaced with fresh solution. Repeated overnight contact on shaker table
7. Decanted off caustic brine solution. Washed zeolite samples three times with 100 mL of deionized water
8. Dried samples at 105°C overnight. After drying, samples were stored in beaker covered with tissue paper to allow for equilibration of the zeolite to atmospheric moisture

The zeolite used in this study was mined at Mount Gipps, some 200 km north of Sydney, Australia. It was essentially clinoptilolite having a bulk density of 1600 kg/m³.



Saturation Capacity of the Zeolite

Saturation ammonium capacity of the zeolite was determined by contacting the virgin or preconditioned zeolite with concentrated solutions of pure ammonium chloride. Different sample sizes were used to check that the results for ammonium adsorption capacity were repeatable and consistent. A variety of zeolite grain sizes were tested. The procedure was as follows:

1. Zeolite samples were weighed into 250 mL conical flasks
2. Standard NH_4Cl solution was prepared by dissolving 5 g of analytical grade NH_4Cl powder in 2000 mL of deionized water. The ammonium concentration of the standard solution was measured using the Hach Nessler method
3. 100 mL of standard NH_4Cl solution (645 mg $\text{NH}_4^+-\text{N/L}$, where NH_4^+-N is the ammonium represented in terms of its nitrogen component only) was added to each flask and to one control flask (no zeolite)
4. Flasks were placed on shaker table in constant temperature room (25°C) overnight
5. After 24 hours, 50 mL of solution was decanted from each flask for analysis, and replaced with 50 mL of fresh standard solution (645 mg $\text{NH}_4^+-\text{N/L}$). The flasks were returned to the shaker for another 24 hours
6. Repeated Steps 4 and 5 until no more exchange of NH_4^+ was measured

Equilibria

Samples of the preconditioned zeolite were used to investigate the binary equilibria relationships with solutions of NH_4Cl , CaCl_2 , MgCl_2 , and KCl . Known concentrations of the salt solutions were prepared by addition of deionized water to analytical grade chloride salts. Adsorption isotherm studies were performed in 250 mL capped conical flasks in the constant temperature room at 25°C, and allowed to equilibrate for at least 7 days. Preliminary studies were performed which revealed that equilibrium was achieved within 3 days contact. A shaker table (rotating at 180 oscillations per minute) was employed to provide constant mixing of the zeolite and solution. Each set of flasks was accompanied by two control flasks prepared without zeolite addition. After 7 days the flasks were removed from the shaker and samples were drawn from each flask, passed through 0.45- μm nylon filters, and triplicate analysis of NH_4^+ or appropriate metals was performed on the solution. Ca^{2+} , Mg^{2+} , and K^+ were analyzed by inductively coupled plasma (ICP) spectrophotometry.



RESULTS AND DISCUSSION

Binary Ion-Exchange Equilibria

The first stage of the binary equilibria study focused on the improved adsorption capacity which might be achieved through chemical pretreatment of the zeolite. By repeatedly exposing a sample to high concentration pure solutions containing one particular cation only, the exchange sites within the crystal structure were made uniform or homo-ionic. The cations used for this study were sodium, calcium, magnesium, and potassium. Virgin zeolite, washed and dried, was also tested.

The influence of the homo-ionic form of the zeolite was shown in the equilibrium isotherms resulting from contact with a range of dilute NH_4Cl solutions. The most favorable adsorption profile for ammonium was achieved by pretreating the zeolite and converting it to the sodium form, based on the equilibrium capacity of the zeolite over the range of solution concentrations studied. The ultimate capacity was also greatest for the sodium form (Table 1). The ion-exchange capacity for ammonium of the sodium-form zeolite was found to be 1.5 meq/g. This compares reasonably well with the data of other workers: 0.65 meq/g for Hungarian clinoptilolite, 2.2 meq/g for Californian clinoptilolite in the sodium form (9), and 2 meq/g for a sodium-pretreated clinoptilolite (10). The ion-exchange capacity of a clinoptilolite depends on the origin of the material and its pretreatment conditions.

The equilibrium isotherm for the sodium zeolite in pure ammonium chloride solutions was constructed from batch equilibrium tests (see Fig. 2). It can be seen from the repeated trials that the isotherm is reproducible for different samples of the sodium pretreated zeolite. This gives credibility to the consistency of performance of the zeolite as an ion-exchange medium.

The effect of zeolite particle size on the equilibria was determined by performing a series of batch tests where all parameters in each set were identical

TABLE 1
Effect of Homo-ionic Form of Zeolite on Ultimate Ammonium
Adsorption Capacity

Homo-ionic form of the zeolite	Ultimate capacity for ammonium, Q° (meq $\text{NH}_4^+ - \text{N/g}$)
Na^+	1.5 ± 0.1
Ca^{2+}	1.1 ± 0.1
Mg^{2+}	1.1 ± 0.1
K^+	1.0 ± 0.1
Virgin zeolite	1.2 ± 0.1



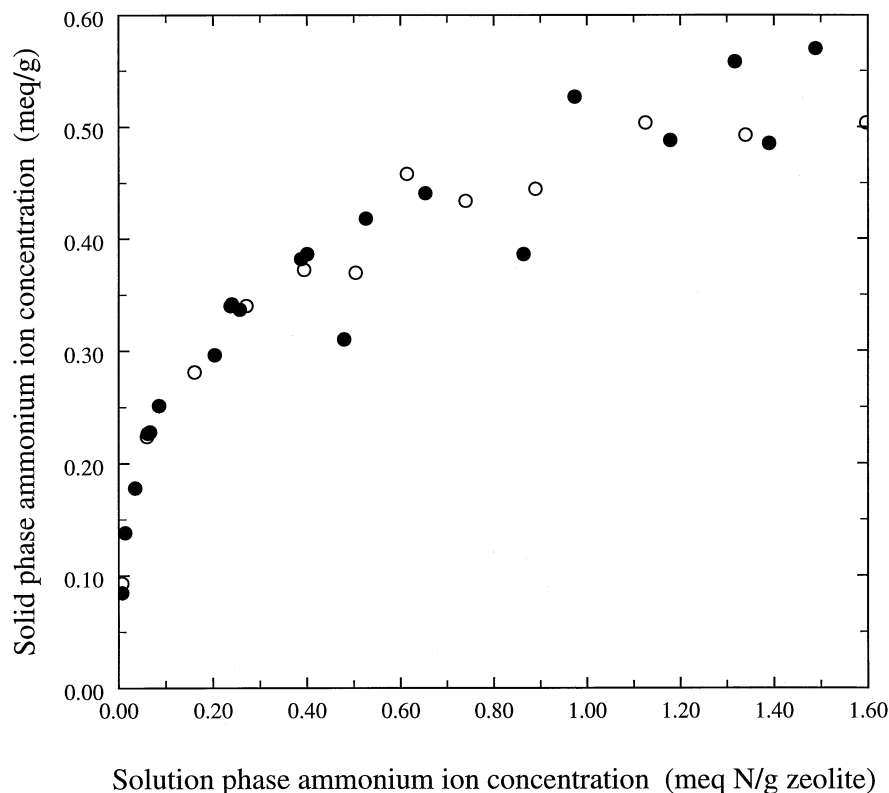


FIG. 2 Equilibrium isotherms for the $\text{NH}_4^+ - \text{Na}^+$ binary ion-exchange equilibrium on zeolite. Two batches.

except the grain size of the zeolite. Figure 3 and Table 2 show the results for this study, which reveal that ion-exchange equilibria between the zeolite and the solution containing ammonium is independent of zeolite particle size. This supports the conclusions derived from studies (11) of the ion-exchange properties of natural zeolite from the United States. The negligible effect of particle size on equilibrium ammonium capacity of the zeolite simplifies the design considerations for a continuous treatment process. It should be noted, however, that Jorgensen and coworkers (8, 12, 13) found that the uptake of ammonia by Hungarian clinoptilolite increased significantly with decreasing particle size. The presence or absence of a variation in the ion-exchange behavior of a clinoptilolite with particle size will depend greatly upon both the origin of the material and its pretreatment.

The application of empirical relationships for describing the binary equilibria between a solution and resin provides a simple technique for prediction of solid and solution equilibrium concentrations. The two most commonly employed types of models are based upon the Langmuir and Freundlich equations. In essence, the Langmuir model is based on the concept of a constant site energy providing a constant cation capacity for each exchange site, and relates the inverse solid concentration to the inverse solution concentration. The

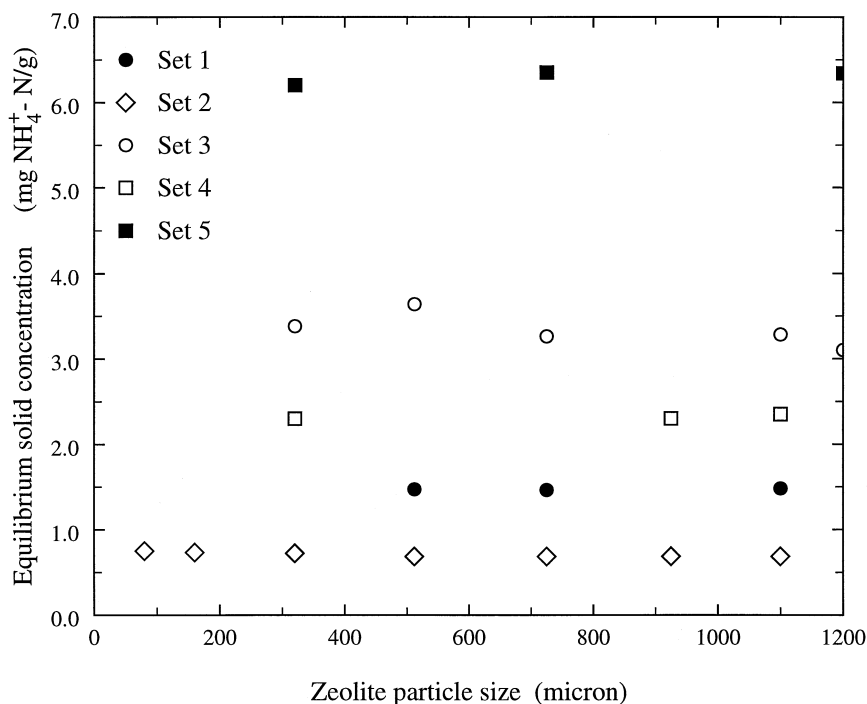


FIG. 3 Effect of zeolite particle size on the $\text{NH}_4^+ - \text{Na}^+$ equilibrium.

Freundlich model describes a logarithmic relationship between the solid and solution concentrations.

Binary equilibria data for the adsorption of ammonium, calcium, magnesium, and potassium onto sodium-pretreated zeolite was successfully applied to the Freundlich model for the purpose of providing a simple relationship between the equilibrium ammonium concentrations in the solution and solid phases. The Freundlich-type equation describes the equilibrium relationship as (14):

$$q = kC^n \quad (1)$$

TABLE 2
Experimental Conditions for Particle Size Tests Shown in Fig. 3

Set	Initial solution concentration (mg $\text{NH}_4\text{-N/L}$)	Solution volume (mL)	Mass of zeolite sample (g)	Initial concentration in solution per mass of zeolite (mg $\text{NH}_4\text{-N/g zeolite}$)
1	23.6	150	5	0.8
2	20	150	2	1.5
3	105	50	2	2.6
4	52	150	2	3.9
5	185	50	1	9.2



where q is the equilibrium ammonium concentration in the solid (i.e., zeolite) phase expressed in meq/g zeolite, and C is the equilibrium ammonium concentration in the solution phase expressed in meq/L.

A linear expression results from taking the \log_{10} of both sides of Eq. (1):

$$\log_{10} q = \log_{10} k + n \log_{10} C \quad (2)$$

where k and n are empirical constants.

The Freundlich equation is useful in correlating isotherm data obtained over a wide range of concentrations. Figure 4 shows the binary equilibria for the $\text{NH}_4\text{-Na}$ presented on a Freundlich plot. The parameters in Eq. (1) were determined by a regression package.

The linear equilibrium relationship for Na-zeolite in pure NH_4Cl solutions is given in Fig. 4. The data may be adequately represented by the expression:

$$q = 0.3156C^{0.388} \quad (3)$$

It is seen that while the data fit the Freundlich plot reasonably well, the equation gives no limit on adsorption of the cation species by the zeolite. The correlation, while obviously limited, gives a quick and simple means for calculating approximate ammonium concentration for one phase (solid or solution) given the other phase concentration. The Freundlich model was found to be suitable for describing the equilibria of the four binary systems ($\text{NH}_4\text{-Na}$, Ca-Na , Mg-Na , and K-Na).

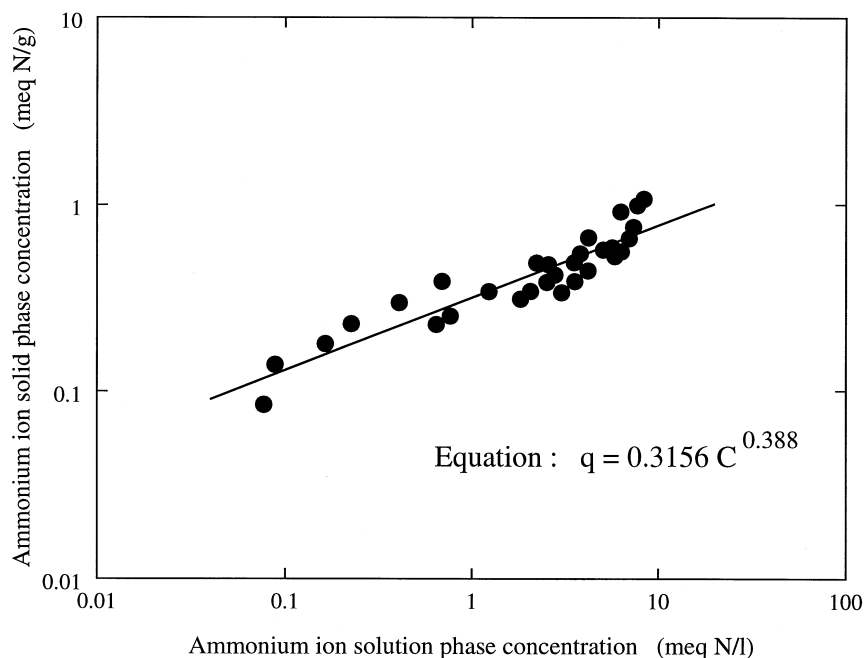


FIG. 4 The Freundlich model applied to the equilibrium for ammonium ions exchanged onto Na-form zeolite.



A more satisfactory description of the binary equilibria relationship between a solution and solid is based on the law of mass action. The equivalent ionic fraction of cation A in the solution phase (X_A) was determined by analytical measurements of initial (C_0) and equilibrium (C_A) solution concentrations, expressed as meq/L, and subsequent calculation from the expression:

$$X_A = C_A/C_0 \quad (4)$$

The zeolite-phase ionic fraction (Y_A) was calculated by mass balance, thus:

$$Y_A = q/Q^\circ \quad (5)$$

where q may be defined by

$$q = \frac{(C_0 - C_A)V_e}{m_e} \quad (6)$$

and Q° is the saturation capacity of sodium zeolite (meq/g zeolite), V_e is the equilibrium solution volume (L), and m_e is the equilibrium mass of zeolite (g).

The selectivity coefficients for these binary equilibria were calculated substituting the equality relationships for binary systems given by:

$$X_A + X_B = 1 \quad (7)$$

$$Y_A + Y_B = 1 \quad (8)$$

giving the following relationship for exchange of the univalent NH_4^+ or K^+ ion with the univalent Na^+ :

$$\alpha_{A,\text{Na}} = \frac{(Y_A/X_A)}{(Y_{\text{Na}}/X_{\text{Na}})} = \frac{Y_A(1 - X_A)}{X_A(1 - Y_A)} \quad (9)$$

For the exchange of divalent calcium or magnesium ions for sodium ions, the selectivity coefficient is calculated as:

$$\alpha_{A,\text{Na}} = \frac{(Y_A/X_A)}{(Y_{\text{Na}}/X_{\text{Na}})^2} = \frac{Y_A(1 - X_A)^2}{X_A(1 - Y_A)^2} \quad (10)$$

where the selectivity coefficient (α_{AB}) shows zeolite preference or nonpreference for ion A over B (15). The selectivity coefficients for the four binary equilibrium systems studied are presented in Table 3. The order of selectivity

TABLE 3
Selectivity Coefficients Obtained from the Binary Equilibria Study

$\alpha_{\text{NH}_4,\text{Na}}$	$\alpha_{\text{Ca},\text{Na}}$	$\alpha_{\text{Mg},\text{Na}}$	$\alpha_{\text{K},\text{Na}}$
0.5–4.0	0.5	0.22	10



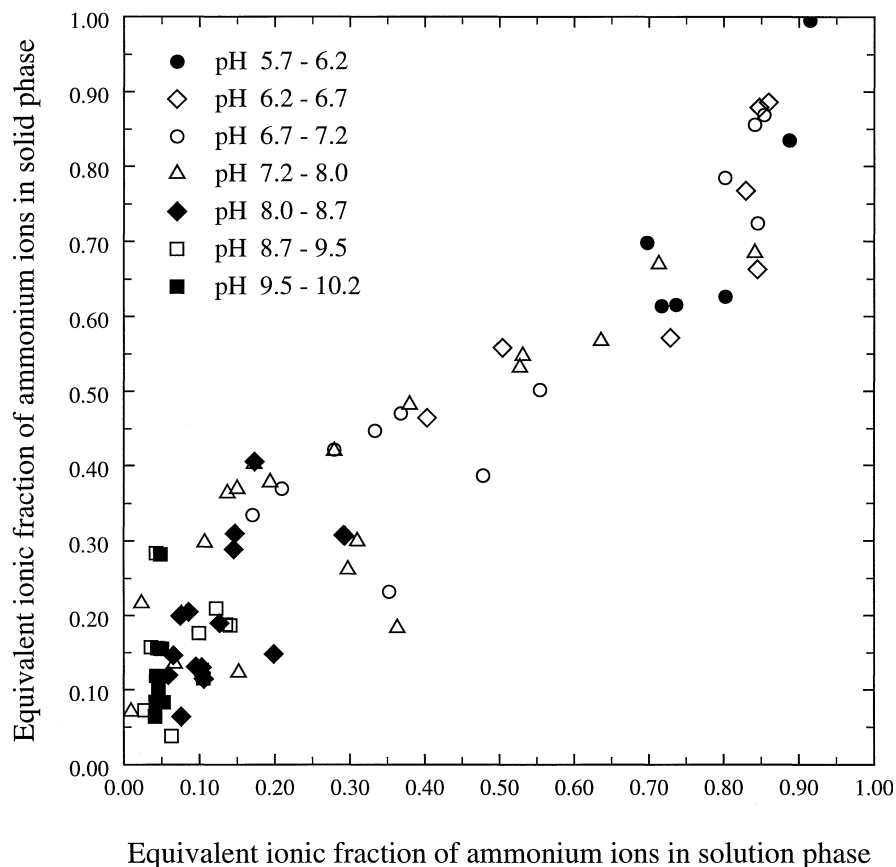


FIG. 5 Effect of equilibrium solution pH on the $\text{NH}_4^+ - \text{Na}^+$ binary isotherm for Na-pretreated clinoptilolite.

of the zeolite for the competing cations agrees with the original findings of Ames (4) for ion selectivity of the particular type of zeolite, clinoptilolite, where: $\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$.

The binary equilibrium isotherm data for ammonium onto Na-form zeolite is presented in Figs. 5 and 6. Figure 5 shows the range of pH values of the equilibrium solution while Fig. 6 shows the effect of the initial solution concentration on the equilibrium data. The isotherm data displays a sigmoid shape but is still reversible, as described by Barrer et al. (3). The selectivity reversal indicated by the curve may be attributed to variations in the relative values of the solution-phase activity coefficients or may be caused by the double ion sieve effect of zeolite as described previously. According to Helfferich (14), certain zeolites contain exchange sites of different types, more simply explained as cages of different dimensions. The ion-exchange characteristics of these sites are unique, and while some cations, e.g., NH_4^+ , may occupy both types of sites, other larger cations may be restricted to exchange with only a



percentage of the overall available sites. The isotherm data presented in Figs. 5 and 6 show that the zeolite has a high selectivity for incoming ammonium ions for around the first 50% of exchange sites filled. As the exchange level increases beyond this point, the selectivity decreases to display unselective behavior for the ammonium ions over the sodium ions.

According to studies performed by Jorgensen (12), the selectivity of sodium-zeolite for ammonium ions is greatly reduced as the solution pH increases above 7. Jorgensen's equilibrium data show that the zeolite is most selective for ammonium at pH 5 ($\alpha_{\text{NH}_4, \text{Na}} = 11.50$), and at pH 7 the selectivity is reduced considerably ($\alpha_{\text{NH}_4, \text{Na}} = 3.35$). The equilibrium isotherm show the zeolite is nonselective for ammonium at pH 9 ($\alpha_{\text{NH}_4, \text{Na}} = 0.563$). Jorgensen (12) attributed the variation in the equilibrium solution pH to the release of OH^- ions remaining in the interstitial water of the zeolite after regeneration. It would therefore be anticipated that the greater the zeolite mass to solution volume ratio in the batch equilibria tests, the greater the equilibrium pH. This is observed for the present study as the final solution pH varies from 5.75 to

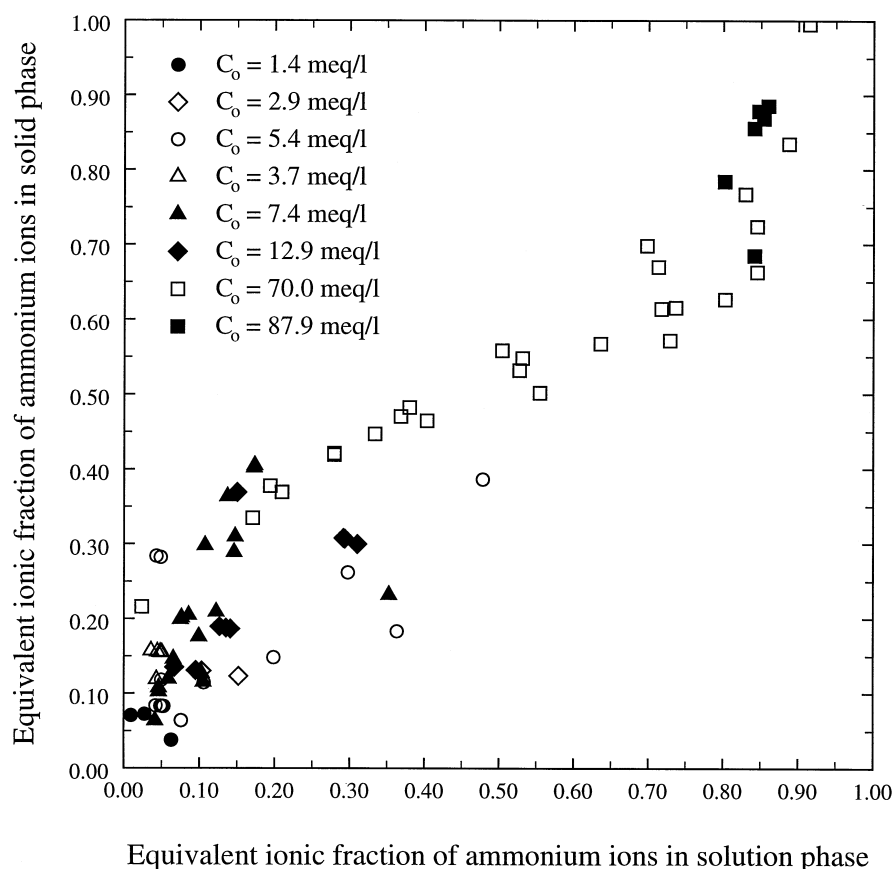


FIG. 6 Effect of initial ammonium concentration on the $\text{NH}_4^+ - \text{Na}^+$ binary isotherm for Na-pretreated clinoptilolite.



10.15, depending on the particular test conditions. It is apparent that neither the final solution pH nor the initial solution concentration can completely account for the deviation of the isotherm toward unselective behavior at $X_{\text{NH}_4} > 0.5$.

The selectivity reversal observed in Figs. 5 and 6 may be explained by reference to Fig. 1 which shows the two types of channels in the zeolite structure. After ammonium has been fully exchanged into the smaller ammonium selective channels, the selectivity of the larger channels becomes significant. Given that the larger channels show less selectivity for ammonium over sodium, two isotherms of the two types of exchange sites would result. The binary isotherm given in Fig. 5 indicates that the zeolite may have behaved in a bifunctional manner, with the resultant isotherm as a superimposition of the isotherms for the two types of exchange sites.

The removal of ammonium from wastewaters, using natural Australian zeolite, is therefore better suited to low concentration effluents. Selectivity of the zeolite for ammonium decreases as the solution ammonium fraction increases. From the binary isotherm curve in Fig. 5, the selectivity of the zeolite for ammonium ions over sodium ions was seen to turn around at about $X_{\text{NH}_4} = 0.5$. This point corresponds to the selectivity coefficient value approaching unity. In practice, the ion-exchange system would be designed to operate with effluent solution ammonium fractions below the point of $X_{\text{NH}_4} = 0.5$ to ensure the most favorable conditions for ammonium uptake by the zeolite. This condition would certainly be maintained for removal of ammonium from influent sewage concentrations averaging 25 mg N/L down to 5 mg N/L, where breakthrough of the ammonium and therefore termination of the loading cycle might occur when $X_{\text{NH}_4} > 0.2$, depending on the other ions in the aqueous phase.

Multicomponent Ion-Exchange Equilibria

Batch experiments using six solutions of differing compositions were undertaken to evaluate the effect of competing cations on the equilibrium capacity of the zeolite. The cations investigated were sodium, calcium, magnesium, and potassium as these are the prevalent cations in treated sewage. Table 4 presents the compositions of the six different solutions studied in the experiments. The results indicate the extent of inhibitory effects of competing cations in the influent solution. Relationships between concentrations of particular cations and the ammonium exchange capacity of the zeolite were studied.

The adsorption of ammonia from the six different multicomponent solutions is presented in Figure 7. The binary isotherm data relating to Feeds 1, 2, and 3 are very similar to one another. While the ammonium equilibrium capacity of the sodium zeolite is least inhibited by the presence of the magne-



TABLE 4
Composition of Multicomponent Systems Studied

Initial solution	Feed 1	Feed 2	Feed 3	Feed 4	Feed 5	Feed 6
NH ₄ -N (meq/L)	1.8	1.9	1.9	1.6	1.4	1.4
Ca (meq/L)	0	3.75	2	0	1.9	0
Mg (meq/L)	4	0	2	2	0	0
K (meq/L)	0	0	0	0.4	0.4	0.8
Na (meq/L)	0	0	0	0	0	0
TOTAL (meq/L)	5.8	5.65	5.9	4	3.7	2.2

sium ions in Feed 1, the presence of the calcium ions in Feed 2 at a concentration similar to the magnesium ion concentration in Feed 1 results in only a slightly increased level of inhibition. These results suggest that magnesium and calcium have similar effects on the ammonium equilibrium capacity of the sodium-zeolite. The presence of the magnesium and calcium ions at the concentrations studied reduced the amount of ammonium ions in the solid (i.e., zeolite) phase by approximately 25%.

The influence of potassium ions on the ammonium uptake by the zeolite is significant, as anticipated by the very high selectivity coefficient ($\alpha_{K,Na} = 10$)

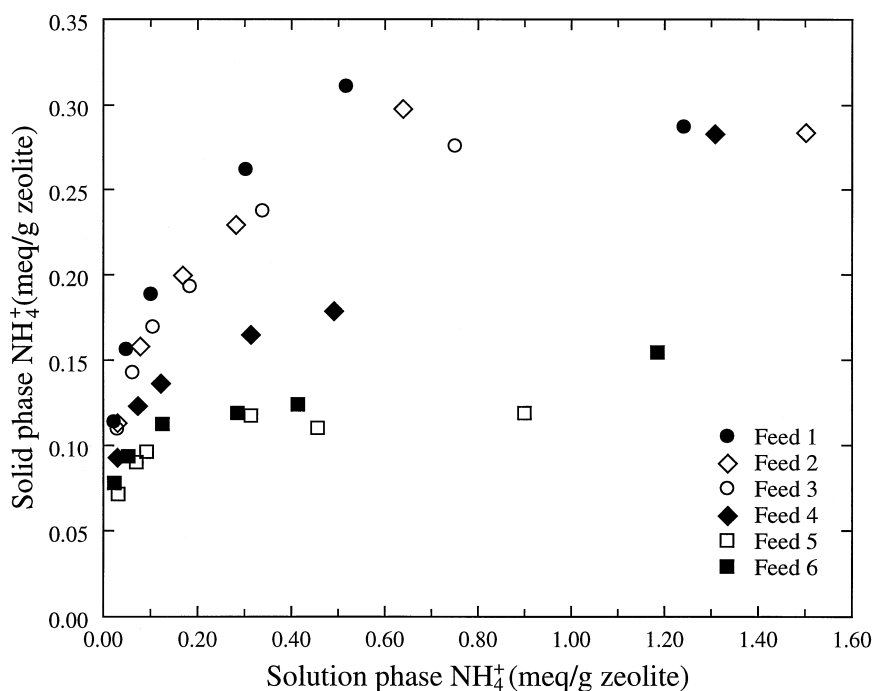


FIG. 7 Adsorption of NH₄⁺ by Na-zeolite from the various multicomponent batch solutions with compositions described in Table 4.



determined from the binary equilibria. The presence of 0.8 meq/L of potassium, as the sole competing cation (Feed 6) initially in solution with 1.4 meq/L of ammonium, causes a significant decrease in the zeolite's ammonium adsorption. The presence of 1.9 meq/L of calcium with just 0.4 meq/L of potassium in Feed 5 gives similar results to Feed 6, indicating the relative degrees to which potassium and calcium inhibit ammonium selectivity by the zeolite. The presence of magnesium in Feed 4 does not give rise to any significant additional inhibition of ammonium adsorption, compared to the inhibition displayed for Feed 6.

A number of approaches can be used to determine the ion-exchange performance of the zeolite in multicomponent systems ranging from the more rigorous approaches of Shallcross et al. (16) to the more empirical approach used by Allen and Addison (17). It was considered adequate for the purpose of this study to apply simple techniques for the prediction of multicomponent equilibria.

If it is assumed that the equilibrium behavior for each binary pair is independent and that there are no multicomponent interactions, then by substituting the binary separation factors into the mass balance relationships,

$$X_A + X_B + X_C + \cdots = 1 \quad (11)$$

$$Y_A + Y_B + Y_C + \cdots = 1 \quad (12)$$

results in a series of expressions for the concentration of each species absorbed on the zeolite as follows:

$$Y_A = \frac{\alpha_{A,Na} X_A}{\alpha_{A,Na} + \alpha_{B,Na} X_B + \alpha_{C,Na} X_C + \cdots} \quad (13)$$

Figures 8 to 13 show the predicted and actual ion-exchange equilibria for ammonia in the multicomponent feed solutions defined in Table 4. Predicted equilibria are determined using Eq. (13). This model is described more fully elsewhere (18). It can be seen that the predicted adsorption of ammonia from the various multicomponent systems correlates well with those obtained experimentally. The agreement between model prediction and experimental observation is poorest for Feed 1, where the influence of magnesium is greater than that predicted using the selectivity coefficients determined from binary equilibria studies. For the other multicomponent systems tested, the accuracy of prediction of corresponding isotherms is reasonable (within 20% for most points). The influence of competing cations depends on the concentrations of each cation present, since their influence varies considerably.

The method outlined for the prediction of ammonium adsorption isotherms for different competing cations provides a convenient technique for assessing the suitability of Australian natural zeolite for ammonium removal from wastewaters. To determine whether ammonium adsorption by the zeolite will



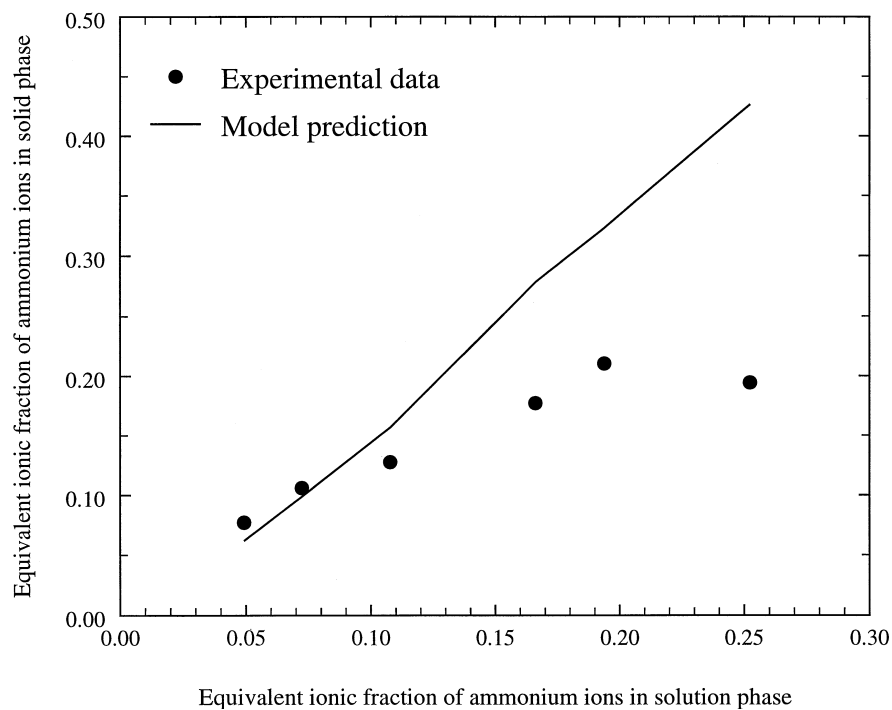


FIG. 8 Comparison between predicted and observed ammonium ion adsorption for Feed 1.

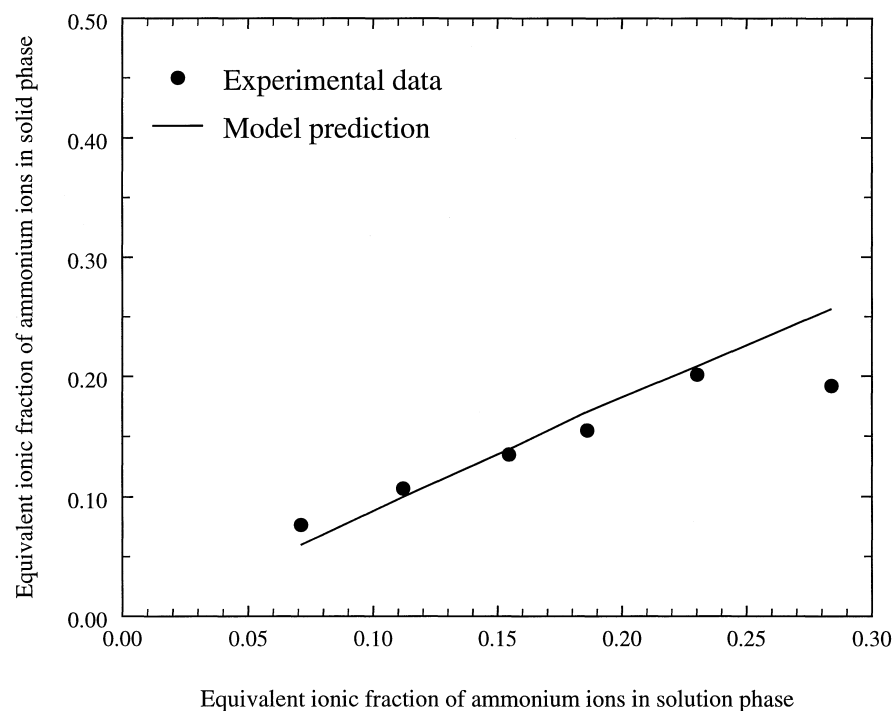


FIG. 9 Comparison between predicted and observed ammonium ion adsorption for Feed 2.



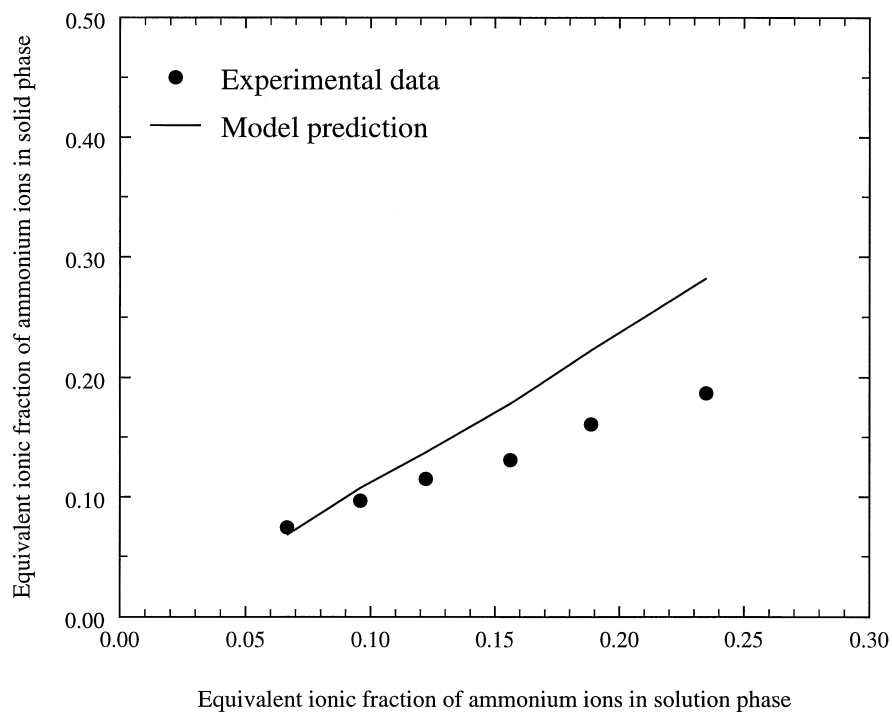


FIG. 10 Comparison between predicted and observed ammonium ion adsorption for Feed 3.

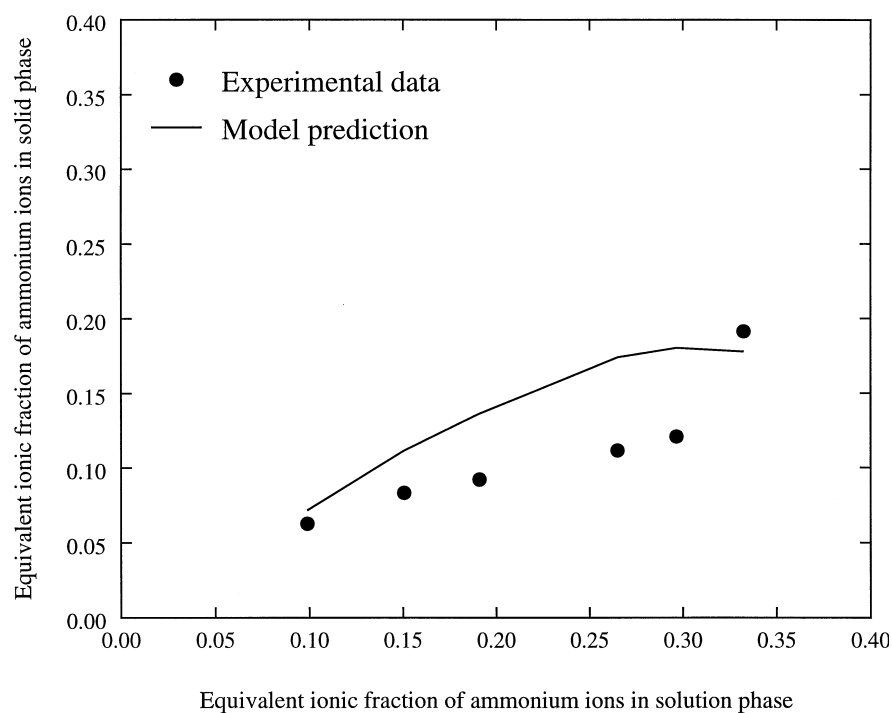


FIG. 11 Comparison between predicted and observed ammonium ion adsorption for Feed 4.



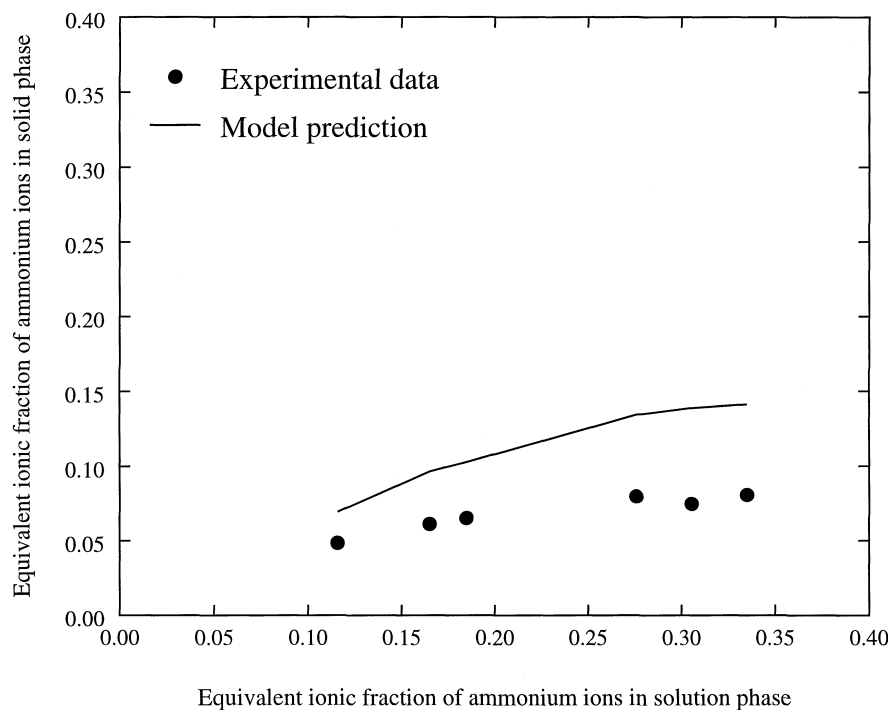


FIG. 12 Comparison between predicted and observed ammonium ion adsorption for Feed 5.

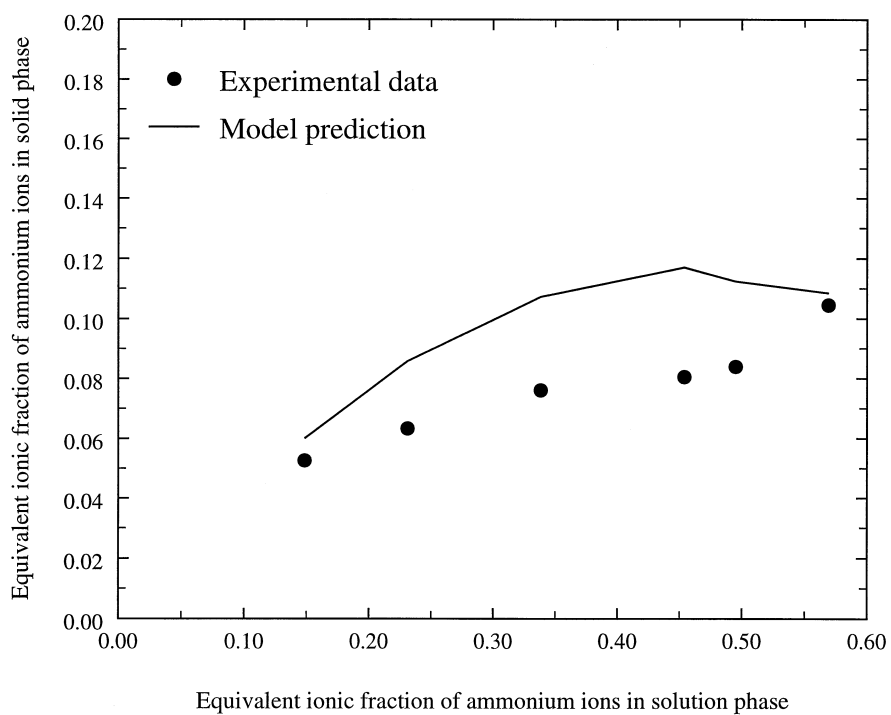


FIG. 13 Comparison between predicted and observed ammonium ion adsorption for Feed 6.



be effective, the cation composition of the influent may be analyzed, and the results applied to the multicomponent equilibria model.

CONCLUSIONS

The laboratory characterization studies revealed some important properties and unique behavior of Australian natural zeolite for solution ammonium removal. Based on the results of this investigation, the following conclusions were reached:

- Equilibrium between the zeolite and the ammonium in solution was independent of zeolite particle size
- The ion-exchange capacity of the zeolite for ammonium was maximized by converting the zeolite to the sodium form. Saturation capacity of the zeolite was experimentally determined as 1.5 meq/g
- Equilibrium between the ammonium and sodium showed ammonium selectivity up to $X_{\text{NH}_4} = 0.5$, above which the selectivity shifted to favor sodium
- Neither solution equilibrium pH nor initial ammonium concentration influenced the selectivity of the zeolite for ammonium; however, the equivalent ammonium fraction in solution at equilibrium, X_{NH_4} , affected the selectivity
- The Freundlich empirical model may be used as a simple method for describing the equilibrium of ammonium, calcium, magnesium, and potassium onto sodium-zeolite.

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